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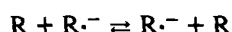
Determination of Rate Constants for the Electroreduction of Aromatic Compounds and Their Correlation with Homogeneous Electron Transfer Rates

Hiroyuki Kojima and Allen J. Bard*

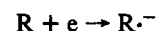
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Abstract: The rate constants for the electroreduction of 16 aromatic compounds, including hydrocarbons, nitriles, nitro compounds, and heterocyclic compounds, at a stationary mercury electrode in *N,N*-dimethylformamide solution were determined. After correction for diffuse double layer effects, the free energies of activation were calculated assuming an adiabatic electron transfer process. They were compared with those for the homogeneous electron exchange reactions which were calculated from reported kinetic data after correction for the diffusional contribution. The results show the existence of the correlation in which the free energies of activation for both the heterogeneous and homogeneous electron transfer reactions are nearly equal, with few exceptions, as predicted by the theories of Marcus and Hush. A correlation was also found between the free energy of activation and the reciprocal of the molecular radius. The absolute values for the free energies of activation, however, differ from those calculated by Marcus theory.

Electron transfer reactions are among the simplest of solution phase reactions and have been the subject of extensive theoretical and experimental studies.¹⁻¹⁹ These reactions involve no breaking or formation of chemical bonds, but rather only changes in the bond lengths and angles and changes in the molecular orientation of the solvent molecules. For the electron exchange reactions of large aromatic molecules, either in homogeneous solution



or at an electrode



the structural changes in the molecules are small, and the major contribution to the energy of activation is solvent reorganization.

Extensive development of the theory of electron transfer reactions has been accomplished by Marcus,² Hush,³ Levich,⁴ Dogonadze,⁵ and many others. The theories of Marcus (and Hush) have been applied most frequently, since the consequences of the theoretical treatments are presented in a form which is conducive to experimental evaluation.

Briefly, these theories make predictions about correlations of various types: (a) between the rate constants for homogeneous electron exchange reactions (or isotopic exchange reactions) and for the cross electron transfer reactions, (b) between the rate constants for electron transfer reactions and the free energies of the reactions, and (c) between the rate constants of homogeneous exchange reactions and electrode reactions.

Experimental studies by Sutin et al.,⁷ Endicott and Taube,⁸ and Aoyagui et al.⁹ have been concerned with experimental verification of the first two of these correlations. The evidence of correlation (c) has been less clear and is the subject of this work.

For outer sphere electron transfer reactions with small internal reorganizations and work terms, so that the solvent reorganization term, λ_0 , is most important, a simple correlation is expected between the rate constants for the homogeneous (k_{ex}) and the heterogeneous (k_s) reactions. According to Marcus² solvent reorganization occurs for two reactant particles in a homogeneous reaction, while it occurs for only one in an electrode reaction, where the "counter particle" is the image charge in the electrode. Under these conditions the following relation applies:

$$k_s/Z_{el} = (k_{ex}/Z_{sol})^{1/2} \quad (1)$$

where Z_{sol} and Z_{el} are the collision numbers for the homogeneous and heterogeneous reactions, respectively. Hush,¹⁰ however, argues that for an electrode reaction, the electrostatic interaction of the reactant particle at its reaction site with its image on the electrode is negligible in the presence of a sufficient concentration of indifferent salt and suggests the following modified correlation:

$$k_s/Z_{el} = k_{ex}/Z_{sol} \quad (2)$$

Experimentally, however, it is not simple to compare these rate constants. For both the homogeneous and the electrode reaction, the measured quantities do not give the inherent electron transfer rate directly. For many homogeneous reactions the rate constant, because it is often so large, involves a contribution from diffusion. For electrode reactions, one must correct the measured rate constant for the effect of the double layer at the electrode on the electron transfer, i.e., information is needed on the location of the reaction site in the vicinity of the electrode and the potential at that location.

There have been few comparisons attempted so far. Marcus¹¹ compared several systems involving metal ions, such as $\text{Fe}(\text{CN})_6^{3-}$ - $\text{Fe}(\text{CN})_6^{4-}$ and MO_4^- - MnO_4^{2-} in aqueous solution. In this comparison, the contribution of the double layer effect on the rate constants was not considered. Moreover some of the systems compared were not clearly simple outer sphere reactions. Malachuk, Miller, Layloff, and Adams¹² studied the homogeneous and electroreduction of nitrobenzene in dimethylformamide (DMF) and in DMF-ethanol; their results were far from the predictions of either eq 1 or 2. Forno, Peover, and Wilson¹³ showed a comparison for aromatic hydrocarbons, such as naphthalene, *trans*-stilbene, and substituted stilbenes in DMF. Although they did not take into account the contribution of diffusion to the homogeneous reaction rates and compared only five systems, they obtained fairly constant values for the ratio k_{ex}/k_s .

The electron transfer reactions of aromatic compounds (e.g., hydrocarbons, nitriles, nitro compounds) appear particularly useful in testing this correlation in outer sphere electron transfers. They form stable radical anions upon reduction in aprotic solvents and conversion from parent to radical anion apparently involves only minor structural

changes. The large size of the molecules also leads to a relatively weak interaction with solvent. There have been appreciable data accumulated for the homogeneous electron transfer reactions of aromatic compounds by the application of ESR.^{9,12-18} However, rather few rate constants for the associated electrode reactions have been reported. The reason for this dearth of heterogeneous rate constants is the difficulty of measurement of these very rapid reactions, especially in the highly resistive aprotic solvents which must be employed to decrease chemical complications caused by reactions of the electrogenerated radical ions.

We present here kinetic data for the electroreduction of aromatic nitriles, nitro compounds, and hydrocarbons in DMF and compare these results to the electron exchange rate constants of the corresponding homogeneous reactions. The correction for the double layer effect was made using diffuse layer theory with the assumption that electron transfer occurs at the outer Helmholtz plane (ohp). The rate constants for homogeneous exchange reactions were corrected for the contribution by diffusion. These rate constants were used to calculate the free energies of activation and thus test theoretical predictions.

Experimental Section

Apparatus. Electron reaction rates were determined by an ac technique employing phase-sensitive detection; experimental details are given elsewhere.²⁰ The technique is similar to other ac bridge and polarographic techniques and involves determination of the amplitude and phase of the ac current at a hanging mercury drop electrode (HMDE) with a lock-in amplifier (Princeton Applied Research, Model HR-8). The ac (sin) wave superimposed on the dc potential had an amplitude of 5 mV; ac frequencies from 425 to 4250 Hz were employed. A two-electrode configuration was employed, with the potential between the HMDE working electrode and a mercury pool counterelectrode controlled with a Wenking Model 61RH potentiostat. The HMDE consisted of a mercury drop (area, 0.03 cm²). It was constructed by sealing a 0.1 mm diameter platinum wire in glass, cutting it off flush with the glass, and gold plating the exposed Pt.²⁰

The HMDE potential was monitored against a saturated aqueous calomel reference electrode (SCE) which was separated from the test solution by two fritted glass disks and an agar salt bridge. *N,N*-Dimethylformamide (DMF) was used as the solvent and tetra-*n*-butylammonium perchlorate (TBAP) was used as supporting electrolyte at a concentration of 0.5 M. All solutions were prepared in a glove-box (Vacuum Atmospheres Corporation, Hawthorne, Calif.) equipped with a Model MO-40-1 Dri-Train. The solutions were degassed by bubbling dry nitrogen through the solutions and the measurements were made under a nitrogen atmosphere at $22 \pm 2^\circ\text{C}$. Each set of measurements was performed twice on the same sample solution, and when necessary, it was repeated with freshly prepared solutions.

Reagents. Benzointrile (Matheson Coleman and Bell), *o*-, *m*-, and *p*-tolunitriles (Aldrich Chemical Co.), and nitrobenzene were purified by distillation under atmospheric pressure. Dibenzofuran, dibenzothiophene, *p*-naphthoquinone, *p*-dinitrobenzene, *m*-nitrobenzointrile (Eastman Organic Chemicals), *m*-dinitrobenzene, anthracene, and perylene (Matheson Coleman and Bell) were purified by recrystallization first from benzene and then from methanol, and were dried for several hours under vacuum. Phthalonitrile, terephthalonitrile (Eastman Organic Chemicals), and 4-cyanopyridine (Aldrich Chemical Co.) were purified by chromatography using benzene on an alumina column, and then recrystallized from benzene and dried. TBAP (Southwestern Analytical Chemicals) was dried under vacuum at 100°C for 2 days and stored under a helium atmosphere in the glove-box. DMF (Matheson Coleman and Bell) was purified by the procedure previously described²⁰ and was stored under a helium atmosphere in the glove-box.

Results

Determination of Kinetic Parameters. For quasireversible electrode reactions with $k_s > 0.02 \text{ cm sec}^{-1}$, the diffusion

Table I. Electrochemical Kinetic Parameters^a

Compd	$E_{1/2}^r, b$ V	$D^{1/2} \times 10^3, c$ cm sec ^{-1/2}	k_s, c cm sec ⁻¹	α	$-\phi_2, d$ mV	$k_{s(\text{corr})}, e$ cm sec ⁻¹
Benzonitrile	-2.17	3.4	$6.1 \pm 0.3 \times 10^{-1}$	0.64 ± 0.03	83	4.9
4-Cyanopyridine	-1.71	2.5	$4.2 \pm 0.2 \times 10^{-1}$	0.54 ± 0.02	73	2.0
<i>o</i> -Tolunitrile	-2.20	3.3	$6.3 \pm 0.3 \times 10^{-1}$	0.59 ± 0.02	84	4.3
<i>m</i> -Tolunitrile	-2.22	3.2	$6.3 \pm 0.3 \times 10^{-1}$	0.57 ± 0.03	85	4.2
<i>p</i> -Tolunitrile	-2.28	3.2	$9.0 \pm 0.3 \times 10^{-1}$	0.59 ± 0.03	86	6.6
Phthalonitrile	-1.57	3.2	1.4 ± 0.1	0.60 ± 0.03	71	7.4
Terephthalonitrile	-1.44	3.0	$6.8 \pm 0.3 \times 10^{-1}$	0.54 ± 0.02	67	2.8
Nitrobenzene	-1.05	3.2	2.2 ± 0.3	0.70 ± 0.05	56	10
<i>m</i> -Dinitrobenzene	-0.76	2.7	2.7 ± 0.5	0.50 ± 0.04	46	6.5
<i>p</i> -Dinitrobenzene	-0.55	2.6	$9.3 \pm 1.0 \times 10^{-1}$	0.61 ± 0.05	36	2.2
<i>m</i> -Nitrobenzonitrile	-0.83	3.0	1.8 ± 0.4	0.60 ± 0.06	49	5.8
Dibenzofuran	-2.41	2.9	2.9 ± 1.0	<i>f</i>	89	21
Dibenzothiophene	-2.37	2.7	1.6 ± 0.5	<i>f</i>	88	12
<i>p</i> -Naphthoquinone	-0.52	2.7	2.1 ± 1.0	<i>f</i>	35	4.6
Anthracene	-1.82	2.6	5 ± 3	0.55 ± 0.04	76	27
Perylene	-1.54	2.4	5 ± 2	0.50 ± 0.10	70	20
Naphthalene	-2.49	3.8	1.0	0.56	145	23
<i>trans</i> -Stilbene	-2.15	2.9	1.2	0.58	139	27
α -Methyl- <i>trans</i> -stilbene	-2.26	2.6	4.3×10^{-1}	0.45	146	5
Hexamethyl- <i>trans</i> -stilbene ^g	-2.46	2.4	1.8×10^{-1}	0.46	145	2.8

^a Obtained by an ac impedance method with the hanging mercury drop electrode at $22 \pm 2^\circ\text{C}$; DMF solution of 0.5 M TBAP. The data of the last four systems were taken from ref 13 (an ac impedance method with the dropping mercury electrode at 30°C ; DMF solution of 0.1 M TBAI). ^b Determined vs. SCE. ^c Estimation of error is discussed in ref 20. ^d The potential of outer Helmholtz plane. ^e Correction of k_s by using eq 11. ^f Cannot be determined. $k_{s(\text{corr})}$ in these systems calculated using the average value of $\alpha = 0.57$. ^g 2,4,6,2',4',6' isomer.

polarization resistance of the faradaic impedance²¹ is given by:

$$R_{\text{dp}} = \frac{4RT \cosh^2(j/2)}{n^2 F^2 A C_o^* (2D_o \omega)^{1/2}} \quad (3)$$

$$j = (nF/RT)(E_{\text{dc}} - E_{1/2}^r) \quad (4)$$

where n is the number of electrons transferred, A is the electrode area, C_o^* is the bulk concentration of the reactant in the oxidized form, D_o is the diffusion coefficient of the oxidized form, ω is the ac angular frequency, E_{dc} is the dc potential, and $E_{1/2}^r$ is the reversible half-wave potential. At $E_{1/2}^r$ R_{dp} has its minimum value, R_{dp}^m , given by:

$$R_{\text{dp}}^m = 4RT/n^2 F^2 A C_o^* (2D_o \omega)^{1/2} \quad (5)$$

The diffusion coefficient can be obtained from the slope of an R_{dp}^m vs. $\omega^{-1/2}$ plot.

The cotangent of the phase angle, ϕ , of the ac current is given by:

$$\cot \phi = 1 + (2\omega)^{1/2} / \lambda \quad (6)$$

$$\lambda = (k_s/D^{1/2})(e^{-\alpha j} + e^{(1-\alpha)j}) \quad (7)$$

$$D = D_o^{1-\alpha} D_r^\alpha \quad (8)$$

where k_s is the rate constant, D_r is the diffusion coefficient of the reduced form, and α is the transfer coefficient. $\cot \phi$ has its maximum value, $[\cot \phi]_{\text{max}}$ at $[E_{\text{dc}}]_{\text{max}}$, where

$$[\cot \phi]_{\text{max}} = 1 + \frac{(2\omega D)^{1/2}}{k_s \{ (\alpha/[1-\alpha])^{-\alpha} + (\alpha/[1-\alpha])^{1-\alpha} \}} \quad (9)$$

and

$$[E_{\text{dc}}]_{\text{max}} = E_{1/2}^r + \frac{RT}{nF} \ln \left(\frac{\alpha}{1-\alpha} \right) \quad (10)$$

The transfer coefficient, α , is obtained from the measurement of $[E_{\text{dc}}]_{\text{max}}$ using eq 10. The rate constant, k_s , is obtained from the slope of a $[\cot \phi]_{\text{max}}$ vs. $\omega^{1/2}$ plot. Typical examples of these measurements for the system of benzonitrile-TBAP in DMF are shown in Figure 1. Measured values of k_s , α , and $D^{1/2}$ for 16 aromatic compounds are given in Table I.

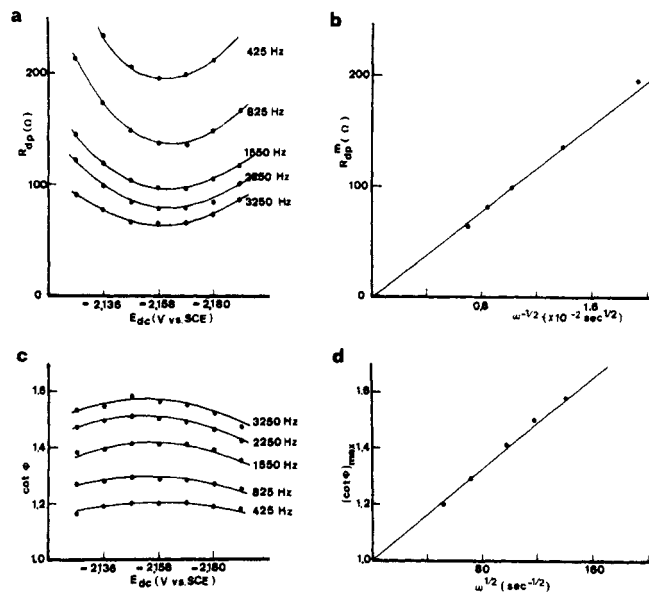


Figure 1. Experimental results for ac measurement of 0.776 mM benzonitrile in DMF-0.5 M TBAP. The HMDE area was 0.0291 cm² and ac frequency was 425 to 3250 Hz. (a) Diffusion polarization resistance, R_{dp} , vs. E_{dc} ; (b) R_{dp}^m vs. $\omega^{-1/2}$; (c) $\cot \phi$ vs. E_{dc} ; (d) $[\cot \phi]_{\text{max}}$ vs. $\omega^{1/2}$.

Correction of the Rate Constant for the Double Layer Effect. When the reaction site (or preelectrode site) is located within the diffuse double layer region, the measured apparent constant must be corrected for the potential drop in this region.²² The correction was made by determining the potential ϕ_2 at the outer Helmholtz plane (ohp) with the assumption that electron transfer occurs at the ohp.²³ The apparent rate constant which is measured is related to the corrected rate constant $k_{s(\text{corr})}$ by the equation²³

$$k_s = k_{s(\text{corr})} \exp((\alpha n - z)F\phi_2/RT) \quad (11)$$

where z is the charge of the reactant. According to the Gouy-Chapman-Stern (GCS) model of the diffuse double layer, ϕ_2 is related to the charge density on the electrode

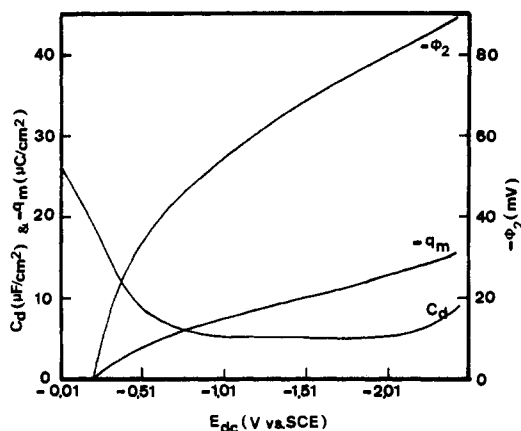


Figure 2. Differential double layer capacity, C_d , charge density, q_m , and calculated potential at OHP, ϕ_2 , for mercury electrode in 0.5 M TBAP in DMF, determined at a frequency of 4250 Hz.

surface, q_m , by the equation

$$\phi_2 = \frac{2RT}{Z_b F} \sinh^{-1} \left\{ \frac{q_m}{(8RT\epsilon C_b)^{1/2}} \right\} \quad (12)$$

where ϵ is the dielectric constant of the bulk solvent, Z_b is the charge of the Z_b - Z_b supporting electrolyte, and C_b is the concentration of the electrolyte. The charge density at a given potential, E , can be obtained from the measured differential double layer capacitance, C_d , by integration from the potential of zero charge, E_z , to E , using eq 13. For the

$$q_m = \int_{E_z}^E C_d dE \quad (13)$$

0.5 M TBAP in DMF solution, E_z was determined from the maximum point of the dropping mercury electrode drop time vs. E curve to be -0.21 V vs. SCE. Experimental values of C_d , q_m , and ϕ_2 for the 0.5 M TBAP-DMF solution are shown in Figure 2. The corrected heterogeneous rate constants, based on these ϕ_2 values, are shown in Table I, with estimated experimental errors for k_s and α . Measurements with compounds **9**, **10**, **15**, and **16** showed a small variation in the measured solution resistance, R_s , near the region of the faradaic reaction, leading to somewhat larger experimental errors for these. The large double layer capacitance of the background solution at potentials where dibenzofuran and dibenzothiophene are reduced interferes with these measurements. The values of $E_{1/2}^r$ in Table I are 50–100 mV more positive than literature values, probably because of differences in the reference electrode liquid junction potential. These differences do not affect the calculated k_s and α values. The values of $D^{1/2}$ for nitrobenzene, *m*-dinitrobenzene, and anthracene are slightly smaller than those reported previously; this difference has been discussed elsewhere.²⁰

Free Energy of Activation for Homogeneous Reaction.

The rate constants for homogeneous electron exchange reactions corresponding to the electrode reactions have been reported by Adams et al., Kowert et al., Peover et al., and Aoyagui et al. and are shown in Table II with the experimental conditions under which the measurements were made. Note that these experimental conditions differ from each other and also from those of the electrochemical measurements. Because the values of k_{ex} approach those of diffusion-controlled reactions, i.e., about $10^{10} M^{-1} \text{sec}^{-1}$, it is necessary to eliminate the diffusional contribution from the measured values.^{14,24} The observed rate constant, k_{obsd} , is related to the activation-controlled rate constant, k_{act} , by the equation

$$1/k_{obsd} = 1/k_{diff} + 1/k_{act} \quad (14)$$

where k_{diff} is the diffusion-controlled rate constant. The quantity k_{act} is the rate constant of interest in correlations with k_s . According to Debye,²⁵ k_{diff} is given by the equation

$$k_{diff} = 4\pi\bar{D} \int_d^\infty \exp(w(r)^r/kT)(dr/r^2) \quad (15)$$

where $w(r)^r$ is the work required to bring the reactant molecules together, d is the distance between the molecules and \bar{D} is the average value of the diffusion coefficients of the reactants. If we assume that $w(r)^r$ is negligible, k_{diff} is reduced to the Smoluchowski equation

$$k_{diff} = 4\pi\bar{D}d \quad (16)$$

The distance d can be considered to equal twice the molecular radius. The molecular radius, a , can be estimated from the density using the equation²⁶

$$(4/3)\pi a^3 = (1/N_0)(\bar{M}/\rho) \quad (17)$$

where N_0 is Avogadro's number, ρ is the density, and \bar{M} is the molecular weight. The calculated values of a , k_{diff} , and k_{act} are summarized in Table II. For those compounds for which ρ values have not been reported, the radius was estimated from the values for similar compounds and the Stokes radius which was obtained from the Stokes-Einstein equation.

The rate constant for the homogeneous exchange reaction is related to the free energy of activation, ΔG_{sol}^* , by eq 18,⁶ where κ is the transmission coefficient and Z_{sol} is the

$$k_{ex} = \kappa Z_{sol} \exp(-\Delta G_{sol}^*/kT) \quad (18)$$

collision number in solution. If we assume an adiabatic process, $\kappa = 1$. Z_{sol} can be estimated from eq 19,⁶ where μ , the

$$Z_{sol} = d^2(8\pi kT/\mu)^{1/2} \quad (19)$$

reduced mass, is equal to $1/2\bar{m}$ for homogeneous R-R⁻ exchange reactions (\bar{m} is the molecular mass). The distance d can again be estimated as twice the molecular radius. Calculated values of Z_{sol} and ΔG_{sol}^* are given in Table III.

The k_{ex} value of perylene has not been reported in DMF solution. However, Suga et al.¹⁵ reported k_{ex} of this compound in dimethoxyethane (DME), and since there is no appreciable difference between the k_{ex} values in DME and DMF according to their results for anthracene, we employ their data in DME solution here. For the case of anthracene, two k_{ex} values have been reported: 4.8×10^8 l./mol sec by Malachuk et al.¹² and 1.8×10^9 l./mol sec by Suga et al.¹⁵ The larger value seems more reasonable, based on the reported values for naphthalene and perylene, and we have employed Suga et al.'s value here.

Free Energy of Activation for Electrode Reaction. The rate constant of the electrode reaction, k_s , is related to the free energy of activation, ΔG_{el}^* , by eq 20,⁶ where Z_{el} is the

$$k_{s(\text{corr})} = \kappa Z_{el} \exp(-\Delta G_{el}^*/kT) \quad (20)$$

collision number at the electrode. Z_{el} can be estimated by eq 21, where \bar{m} is the mass of the reacting molecule. The

$$Z_{el} = (kT/2\pi\bar{m})^{1/2} \quad (21)$$

Z_{el} and ΔG_{el}^* values calculated from $k_{s(\text{corr})}$ from (20) and (21) are summarized in Table III. In addition to our results, the last four systems were calculated using the data of Forno, Peover, and Wilson¹³ which were obtained under slightly different experimental conditions.

In Figure 3, ΔG_{el}^* is plotted vs. ΔG_{sol}^* for the corresponding homogeneous reaction; the number affixed to each dot corresponds to the system numbered in Table III. The data of Forno et al. are represented by the open circles. The

Table II. Rate Constants for Homogeneous Electron Exchange Reactions^a

Compd	k_{ex} , l./ (mol sec)	Ref	Conditions ^b	k_{diff} , ^c l./ (mol sec)	k_{act} , ^d l./ (mol sec)
Benzonitrile	5.5×10^8	14	0.1 M TBAP, 23 ± 2°C	6.0×10^9	6.1×10^8
4-Cyanopyridine	6.8×10^8	14	0.1 M TBAP, 23 ± 2°C	3.0	8.8×10^8
<i>o</i> -Tolunitrile	8.6×10^8	14	0.1 M TBAP, 23 ± 2°C	5.9	1.0×10^9
<i>m</i> -Tolunitrile	5.6×10^8	14	0.1 M TBAP, 23 ± 2°C	5.6	6.2×10^8
<i>p</i> -Tolunitrile	7.8×10^8	14	0.1 M TBAP, 23 ± 2°C	5.6	9.1×10^9
Phthalonitrile	1.2×10^9	14	0.1 M TBAP, 23 ± 2°C	5.5	1.5×10^9
Terephthalonitrile	1.4×10^9	14	0.1 M TBAP, 23 ± 2°C	4.8	2.0×10^9
Nitrobenzene	3.0×10^7	12	0.01 M TEAP, 25°C	5.3	3.0×10^7
<i>m</i> -Dinitrobenzene	5.2×10^8	12	0.01 M TEAP, 25°C	3.8	6.0×10^8
<i>p</i> -Dinitrobenzene	6.0×10^8	12	0.01 M TEAP, 25°C	3.5	7.2×10^8
<i>m</i> -Nitrobenzonitrile	1.6×10^8	12	0.01 M TEAP, 25°C	4.8	1.7×10^8
Dibenzofuran	1.6×10^9	14	0.1 M TBAP	4.9	2.4×10^9
Dibenzothiophene	1.2×10^9	14	0.1 M TBAP	4.0	1.7×10^9
<i>p</i> -Naphthoquinone	4.2×10^8	12	0.01 M TEAP	4.8	4.6×10^8
Anthracene	1.8×10^9	15	Without salt, 25°C	3.9	3.3×10^9
Perylene	2.1×10^9	15	Without salt, 25°C, DME as the solvent	3.7	4.8×10^9
Naphthalene	6.2×10^8	13	0.1 M TBAI, 20°C	7.7	6.7×10^8
<i>trans</i> -Stilbene	1.0×10^9	13	0.1 M TBAI, 20°C	5.0	1.3×10^9
α -Methyl- <i>trans</i> -stilbene	1.4×10^8	13	0.1 M TBAI, 20°C	4.4	1.4×10^8
Hexamethyl- <i>trans</i> -stilbene ^e	6.0×10^7	13	0.1 M TBAI, 20°C	4.1	6.1×10^7

^a Rate constants for the reaction $R^{\cdot-} + R \rightleftharpoons R + R^{\cdot-}$; taken from ref 12–15. ^b DMF solution except the perylene system, where dimethoxyethane (DME) was used. ^c Diffusion-controlled rate constant; calculated by eq 16. ^d Activation-controlled rate constant; calculated by eq 14. ^e 2,4,6,2',4',6' isomer.

Table III. Free Energies of Activation

No.	Compd	Z_{el} , ^a cm sec ⁻¹	ΔG_{el} *, ^b eV	Z_{sol} , ^a l./ (mol sec)	ΔG_{sol} *, ^b eV	ρ , g/cm ³	a , ^c Å
1	Benzonitrile	6.2×10^3	1.84×10^{-1}	3.2×10^{11}	1.61×10^{-1}	1.00 ^{d1}	3.4
2	4-Cyanopyridine	6.2	2.07	2.7	1.47	1.27 ^{d2}	3.2
3	<i>o</i> -Tolunitrile	5.8	1.85	3.2	1.49	0.99 ^{d3}	3.6
4	<i>m</i> -Tolunitrile	5.8	1.86	3.3	1.61	0.98 ^{d4}	3.6
5	<i>p</i> -Tolunitrile	5.8	1.74	3.3	1.52	0.96 ^{d4}	3.6
6	Phthalonitrile	5.6	1.70	3.0	1.36	1.13 ^{d5}	3.6
7	Terephthalonitrile	5.6	1.95	3.0	1.29		(3.5) ^e
8	Nitrobenzene	5.7	1.63	2.9	2.36	1.20 ^{d6}	3.4
9	<i>m</i> -Dinitrobenzene	4.8	1.70	2.5	1.55	1.57 ^{d7}	3.5
10	<i>p</i> -Dinitrobenzene	4.8	1.98	2.5	1.50	1.61 ^{d8}	3.5
11	<i>m</i> -Nitrobenzonitrile	5.2	1.75	2.7	1.90		(3.5) ^e
12	Dibenzofuran	4.6	1.39	2.9	1.24	1.29 ^{d9}	3.8
13	Dibenzothiophene	4.8	1.54	2.8	1.31	1.35 ^{d10}	3.7
14	<i>p</i> -Naphthoquinone	5.0	1.80	2.7	1.64	1.42 ^{d11}	3.5
15	Anthracene	4.7	1.33	3.0	1.15	1.25 ^{d12}	3.8
16	Perylene	3.9	1.36	3.0	1.06	1.32 ^{d13}	4.3
17	Naphthalene	5.6	1.41	3.0	1.56	1.15 ^{d14}	3.5
18	<i>trans</i> -Stilbene	4.7	1.33	3.0	1.41	1.16 ^{d15}	3.9
19	α -Methyl- <i>trans</i> -stilbene	4.5	1.75	3.6	2.00		(4.3) ^e
20	Hexamethyl- <i>trans</i> -stilbene ^f	3.9	1.86	3.7	2.24		(4.7) ^e

^a Collision number defined by eq 19 or 21. ^b Free energy of activation calculated from eq 18 or 20. ^c Molecular radius calculated from eq 17. ^d Density: (1) "Handbook of Chemistry and Physics", 51st ed, Chemical Rubber Publishing Co., Cleveland, Ohio, 1970; (2) *Acta Crystallogr., Sect. A*, 27, 1986 (1971); (3) *Z. Phys. Chem.*, 16, 218 (1900); (4) *Recl. Trav. Chim. Pays-Bas*, 20, 160 (1900); (5) *J. Am. Chem. Soc.*, 70, 2650 (1948); (6) *Z. Anorg. Chem.*, 199, 91 (1931); (7) *Can. J. Res., Sect. B*, 25, 216 (1947); (8) *Indian J. Phys.*, 8, 147 (1933); (9) *Acta Crystallogr., Sect. B*, 28, 1002 (1972); (10) *J. Chem. Soc. A*, 1561 (1970); (11) *Acta Crystallogr.*, 18, 179 (1965); (12) *ibid.*, 3, 245 (1950); (13) *Proc. R. Soc. London, Ser. A*, 279, 129 (1964); (14) *Acta Crystallogr.*, 2, 233 (1949); (15) *J. Chem. Soc.*, 364 (1938). ^e Estimated value; see text. ^f 2,4,6,2',4',6' isomer.

dashed and the solid lines represent the theoretical prediction of eq 1 and 2, i.e.,

$$\Delta G_{el}^* = \Delta G_{sol}^*/2 \quad (22a)$$

and

$$\Delta G_{el}^* = \Delta G_{sol}^* \quad (22b)$$

Discussion

Existence of the Correlation. The results in Figure 3 show a rather scattered distribution at first glance. However, there are some groups which systematically deviate from the main distribution. First, the open circles of Forno et al.'s data¹³ are systematically distributed slightly below the solid line. Their experiment was performed at 30°C with 0.1 M

TBAI as the supporting electrolyte, so that the smaller values of ΔG_{el}^* might be explained in terms of this difference in experimental conditions. For example, ΔG_{el}^* decreases with an increase in temperature and TBAI solutions show much larger differential capacitance at Hg compared to TBAP; this leads to an increase in the magnitude of ϕ_2 resulting in the decrease of ΔG_{el}^* . The two methyl-substituted stilbenes (systems 19 and 20) involve appreciable steric hindrance.²⁷ In such a case, the work needed to bring the reactant to the reaction site cannot be neglected, which also would cause a deviation from a correlation in which work terms are neglected. The triangles, 4-cyanopyridine (2), terephthalonitrile (7), and *p*-dinitrobenzene (10), are distributed together far above the solid line. The k_s values for these are much smaller than those expected from similar

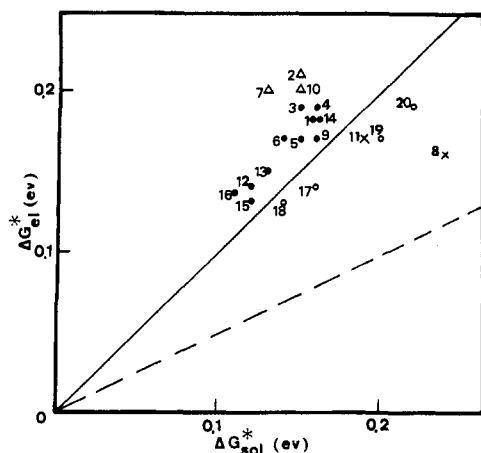


Figure 3. Comparison of experimental activation energies of heterogeneous (ΔG_{el}^*) and homogeneous (ΔG_{sol}^*) electron transfer reactions. Numbers correspond to compounds listed in Table III: (●) results of this study; (Δ) compounds with two electron-attracting groups para to one another; (○) data of Peover et al.; (X) data where k_{ex} is uncertain. Solid line represents theoretical prediction of eq 22b and broken line that of eq 22a.

compounds. A common factor in all of these compounds is the occurrence of two electron-attracting groups in para positions. Terephthalonitrile and *p*-dinitrobenzene have been reported to show abnormally large polarizations, although they have very small permanent dipole moments.²⁸ The reason for the small rate constant can perhaps be explained in terms of a stabilization due to induced polarization under the strong electric field at the electrode. Finally, nitrobenzene (8) and *m*-nitrobenzonitrile (11) deviate far from the main distribution. However, the experimental k_{ex} values for these systems appear questionable to us, i.e., the values of k_{ex} of nitrobenzene and *m*-nitrobenzonitrile are much smaller than those of benzonitrile or *m*-dinitrobenzene. These results were obtained from ESR line broadening in systems which have many hyperfine interactions;¹² recall that the k_{ex} value for anthracene obtained in that study was also much smaller than that reported by Suga et al.^{9a} based on similar ESR measurements. If we eliminate these questionable systems from Figure 3, the remaining points seem to be well distributed near although slightly above the solid line (considering the assumptions and approximations, both theoretical and experimental, that have been made). Moreover the free energies of activation are relatively insensitive to errors in the experimental k values and the choice of Z_{el} and Z_{sol} .

It is very difficult to extend the region of free energy of activation much beyond the range of these measurements. The lower limit is determined by the reactions approaching diffusion control and being difficult to measure precisely, while reactions with higher free energies of activation probably do not conform to the simple outer sphere mechanism.

Within the assumptions of a simple adiabatic outer sphere electron transfer mechanism, we conclude that the experimental results conform more closely to the Hush¹⁰ model for heterogeneous electron transfer (unity slope), rather than the Marcus model (slope of 0.5). Of course one could argue that the data also would fit a line with a slope of one-half, allowing for an intercept of the order of 0.1 eV on the ΔG_{el}^* axis. However, this would require an additional work term in the heterogeneous reaction of quite a large value compared to the overall free energy of activation for all of the reactions; it is difficult to see the origin of such a term.

Treatment of Data. The important assumptions in our data treatment are: (a) that the reaction site is the ohp and

that the potential at that site, ϕ_2 , can be estimated using the Gouy-Chapman-Stern (GCS) diffuse double layer theory, (b) that Z_{el} and Z_{sol} can be employed as preexponential factors, and (c) that there is a negligible contribution of work terms to the free energies of activation. (The work due to the potential difference between the preelectrode site and the bulk solution is taken care of by the Frumkin correction.)

As to assumption (b), there seems no other more reasonable way to estimate these for the assumed adiabatic processes. At least, the collision numbers give a reasonable order of magnitude for the rate constant.²⁹ There is also support for the processes being adiabatic ones.^{6,30}

Assumption (a) has a large effect upon the calculation of ΔG_{el}^* . Peover and Powell³¹ neglected this double layer correction in correlating the apparent rate constants for the electroreduction of a series of nitro compounds with ESR coupling constants, since the range of electrode charge for the series of compounds was relatively small. Peover and co-workers^{13,27} did make such corrections in correlations of k_s and k_{ex} . Hale³⁰ also calculated the absolute value for ΔG_{el}^* for a number of inorganic and organic species neglecting the potential difference between the reaction site and the bulk solution (i.e., by assuming that the reactant was far enough outside the ohp that coulombic work terms could be neglected). He obtained very good agreement with the experimental activation energies in most cases. The importance of this electrostatic work term can be gauged from a consideration of the transfer coefficient, α . According to Marcus α is given by the equation

$$\alpha = (1/2) + (\Delta G_r^0 + w^r - w^p)/2\lambda \quad (23)$$

where λ is a reorganization energy term, ΔG_r^0 is the free energy of reaction at the reaction site, and w^r and w^p represent the work needed to bring the reactant and the product to the reaction site from the bulk. w^r and w^p can be estimated for the electrode reaction from

$$w^r = Ze\phi_2 \quad (24a)$$

$$w^p = Z'e\phi_2 \quad (24b)$$

where Z and Z' are the charges of the reactant and product, respectively. For the $R/R^{\cdot-}$ reaction $\Delta G_r^0 = 0$, $w^r = 0$, and $w^p > 0$, so that α should always be larger than 0.5. The experimental values in Table I are qualitatively in agreement with this prediction, except for the methyl-substituted stilbenes which involve appreciable steric hindrance. This agreement suggests that correction for the potential difference between the reaction site and the bulk solution is necessary. The problem rather exists in the accuracy of the diffuse double layer theory and the location of the reaction site. Although the applicability of the GCS theory has been debated, the results obtained using this model appear satisfactory in the absence of specific adsorption and for reduction potentials fairly negative of the potential of zero charge.²³ Hazelrigg and Bard³² found no specific adsorption for 9,10-diphenylanthracene and several activated olefins and their radical anions in DMF using the chronocoulometric method. Similarly Peover³³ reported no specific adsorption of *trans*-stilbene and its radical anion in DMF. Dietz and Peover²⁷ showed that $k_{s(\text{corr})}$ is constant, within 10%, when the concentration of the supporting electrolyte, TBAI, was varied from 0.1 to 0.7 M for the reduction of *cis*-stilbene, tetracene, and methyl-substituted stilbenes in DMF solution. They also showed that α values which were obtained from the slope of the $\log k_s$ vs. ϕ_2 curve with variation of supporting electrolyte concentration using (11) were in good agreement with those obtained from the potential difference between $[E_{dc}]_{\text{max}}$ and $E_{1/2}^r$ using (10).

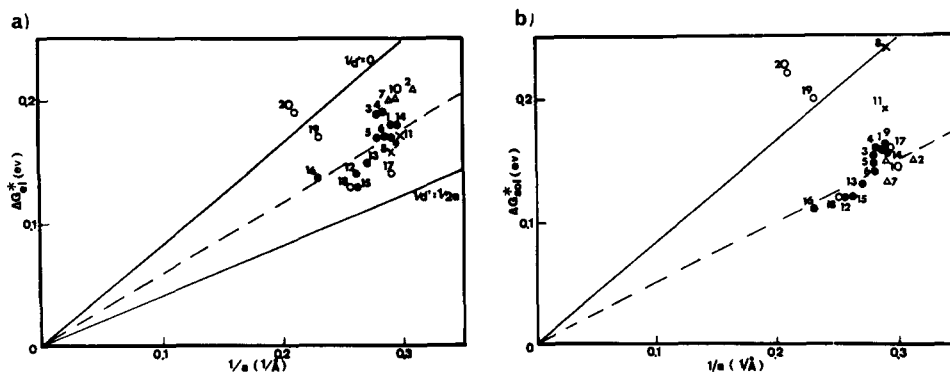


Figure 4. Dependence of activation energies of heterogeneous (ΔG_{el}^*) and homogeneous (ΔG_{sol}^*) reactions on the reciprocal of the molecular radius ($1/a$): (a) ΔG_{el}^* vs. $1/a$; (b) ΔG_{sol}^* vs. $1/a$. Solid line represents theoretical prediction of eq 30.

These results suggest that TBAI is not appreciably adsorbed and that the GCS theory provides a good approximation for the system of aromatic hydrocarbons in TBAP-DMF solution. One of the defects of the GCS theory is that the dielectric constant at the inner layer is assumed to be equal to the bulk value. The bulk value reflects a cluster consisting of three or four molecules, because it is much larger than that expected for isolated molecules from the theory of dispersion.³⁴ Therefore, one would expect the dielectric constant of the inner layer, where a solvent monolayer is formed, to be much smaller than the bulk value. A smaller value would lead to a decrease of ΔG_{el}^* via an increase of $|\phi_z|$. This may explain some of the deviation of the distribution from the solid line. However, there is no reliable estimate of the dielectric constant of the inner layer. Finally we might point out that if, in the comparison of ΔG_{el}^* and ΔG_{sol}^* , the double layer correction is not made, the ΔG_{el}^* values would become much larger than those given in Figure 3 and the distribution would deviate even more from the solid line, as well as the broken line.

As to assumption (c), we can consider three kinds of work: the interaction of the reactants (or products) with each other (including the electrode as the counterpart), the interaction with the solvent, and the interaction with the supporting electrolyte. For the last two types of interactions, hydrogen bonding and the ion pairing are important. Abnormally small values of D for 4-cyanopyridine and *p*-naphthoquinone in Table I can perhaps be attributed to the existence of a hydrogen-bonding interaction. However, this contribution will not be very different in the heterogeneous electrode and homogeneous reactions. The effect of ion pairing cannot be neglected. Hirota et al.³⁵ showed that electron exchange rate decreases with an increase in the strength of ion pairing. Furthermore, TBAP and TBAP are not completely dissociated in DMF solvent ($K_a \approx 4.5 \times 10^{-1}$ for TBAI).³⁶ Our electrochemical measurements were made with 0.5 M TBAP, while the measurements of homogeneous reactions were made with 0.1 M TBAP by Kowert et al.,¹⁴ with 0.1 M TBAI by Forno et al.,¹³ and Malachuk et al.,¹² and without salt by Suga et al.⁹ According to Forno et al.¹³ k_{ex} for *trans*-stilbene in DMF was $10.4 \times 10^8 M^{-1} \text{sec}^{-1}$ with 0.1 M TBAI, and $7.5 \times 10^8 M^{-1} \text{sec}^{-1}$ with 0.5 M TBAI. Since our electrochemical measurements were made in 0.5 M TBAI (to reduce the solution resistance) and the homogeneous rate constants were measured in 0.1 M TBAI, if this difference in k_{ex} attributable to ion pairing is generally the same for all of the couples considered, this would introduce an additional contribution of about 0.007 eV to ΔG_{el}^* compared to ΔG_{sol}^* . This would not make much difference in the correlation, although it may be a contributing factor to the deviation of the experimental results from the solid line.

The interaction of the reactants (or products) with each other can probably be neglected for the homogeneous reactions. The coulombic interaction is zero, because one of the reactants is uncharged. Dimerization between R and R⁻ is possible, but has not been observed in these systems by ESR or electrochemical measurements. This interaction may be of importance in reactions of R with R⁺. In the case of the electrode reaction, the interaction with the electrode can also be neglected with a sufficient concentration of supporting electrolyte as far as we assume that the electron transfer occurs at the ohp or at a larger distance. However, if the reaction site were located within the compact layer, the interaction could not be neglected. There would be an interaction with an image force in the electrode, as well as a loss of solvation energy due to penetration of reactant into the saturated dielectric medium of the compact layer.³⁰ These energy losses should occur even at a potential where the reaction rate is diffusion controlled. Under those circumstances the observed diffusion coefficient should involve an appreciable contribution of this work, because the diffusion barrier is only of the order of 0.1 eV. Generally, however, the D values obtained by electrochemical methods are the same as those obtained by conductivity and other homogeneous solution methods. Thus we conclude, in agreement with previous studies,^{13,33} that the reaction site is not located within the compact layer, and perhaps is even located further out in the diffuse layer than the ohp.

Correlation with Reactant Radius. According to the theory of Marcus,⁶ the free energy of activation is given by the equations

$$\Delta G^* = w^r + m^2 \lambda \quad (25)$$

$$m = -[1/2 + (\Delta G_r^0 + w^p - w^r)/2\lambda] \quad (26)$$

$$\lambda = \lambda_o + \lambda_i \quad (27)$$

$$(\lambda_o)_{sol} = \left(\frac{1}{2a_1} + \frac{1}{2a_2} - \frac{1}{d} \right) \left(\frac{1}{D_{op}} - \frac{1}{D_s} \right) (ne)^2 \quad (28)$$

$$(\lambda_o)_{el} = (1/2) \left(\frac{1}{a_1} - \frac{1}{d'} \right) \left(\frac{1}{D_{op}} - \frac{1}{D_s} \right) (ne)^2 \quad (29)$$

where a_1 and a_2 are the radii of the reactant molecules, d is the mean distance between the center of the reactants in the activated complex for the homogeneous reaction, and d' is the mean distance between the center of the reactant and its mirror image in the electrode; n is the number of electrons transferred in the reaction, and D_s and D_{op} are the static dielectric constant and the optical dielectric constant. The inner sphere energy, λ_i , is the contribution from the changes in bond lengths and angles in the molecule. For the R/R⁻ systems considered here this contribution is probably small; Hale estimated this contribution to be about 5% of the total free energy for aromatic compounds³⁰ unless an

appreciable configurational change occurs. We neglect this term here. For our reactions, $n = 1$, $a_1 = a_2 = a$, and $\Delta G_r^0 = 0$. If we neglect both the work terms and assume that $d = 2a$ for the homogeneous reaction, then the free energy of activation becomes

$$\Delta G_{\text{sol}}^* = \left(\frac{1}{2}\right)^2 \frac{e^2}{2a} \left(\frac{1}{D_{\text{op}}} - \frac{1}{D_s} \right) \quad (30)$$

The expression for the electrode reaction depends upon the choice of d' . If we assume, as Hush³ and Peover³³ do, that the reaction site is at or beyond the ohp and that the image forces in the electrode are unimportant because of screenings by the double layer, the $1/d'$ term is negligible and $\Delta G_{\text{el}}^* = \Delta G_{\text{sol}}^*$, and is given by (30). If d' is taken as $2a$, as is usually given in Marcus' theory, then $\Delta G_{\text{el}}^* = \Delta G_{\text{sol}}^*/2$. In either case, and for homogeneous reactions, the free energy of activation should be proportional to the reciprocal of the radius of the molecule. Figure 4 shows plots of ΔG_{el}^* and ΔG_{sol}^* vs. $1/a$ for the systems studied here, with the values of a taken from Table III. The solid lines represent the theoretical prediction (taking $D_{\text{op}} = 2.04$ and $D_s = 36.7$) and the broken lines represent the experimental ones which were roughly estimated from the distributions of the points. From these plots, we can see that an overall correlation seems to exist, the correlation for the electrode reactions is much poorer than that for homogeneous reactions, and the slope of lines of the correlation is much smaller than the theoretical one. The points which show large deviations from the dashed lines correspond to compounds which also deviate from the plot in Figure 3. The two sterically hindered methyl-substituted stilbenes show an especially large deviation. The reason for the poor correlation for the electrode reactions can be ascribed to the effect of the field in the double layer region. Thus the heterogeneous rate constants for terephthalonitrile, 4-cyanopyridine, and *p*-dinitrobenzene are anomalously small, while there is no appreciable abnormality in that for the homogeneous reactions. The molecular fine structure is probably more significant for electrode reactions than for homogeneous ones. The Marcus equation is based on the assumption that the molecule is a spherical metal conductor with a uniform charge distribution. In a strong electric field, the effect of the induced dipole moment as well as the permanent dipole moment cannot be neglected. The ratio of the slopes between the experimental and the theoretical curves is about 0.60. The Born formula, on which the Marcus equation is based, reportedly yields too high values for the solvation energy when the crystallographic radius is used for the molecular radius.³⁷ In fact, this deviation becomes about 20% for alkaline earth cations. However, for large organic anions, the Born formula was found to be a good approximation.²⁶ For example, the solvation energies calculated by the Born method and estimated from the standard potentials agree within 5% for naphthalene and anthracene radical anions. Levich, Dogonadze, and their coworkers have developed the polaron theory for the solvation reorganization energy;^{4,5,38} the energy required in this theory is less than that of the λ_0 of Marcus' theory, because of the presence of frequency dispersion of the polarization waves. The presence of frequency dispersion involves a correlation of the orientational motion of the dipole moments among the solvent molecules. In

such a case, the solvent polarization is less affected by the presence of the charge of reactant, so that the solvation reorganization energy is smaller. In fact, their calculation for the solvation energy of alkaline earth halides in aqueous solutions was in good agreement with the experimental results. However, the ratio of the theoretical value to the Born formula is about 0.80, which is still insufficient to explain the present results. Unfortunately, their formalism does not lead easily to numerical calculations, so that an application of their theory was not possible for the reactions considered here.

Acknowledgment. Support of this research by National Science Foundation (Grant GP-31414X) and Robert A. Welch Foundation is gratefully acknowledged.

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